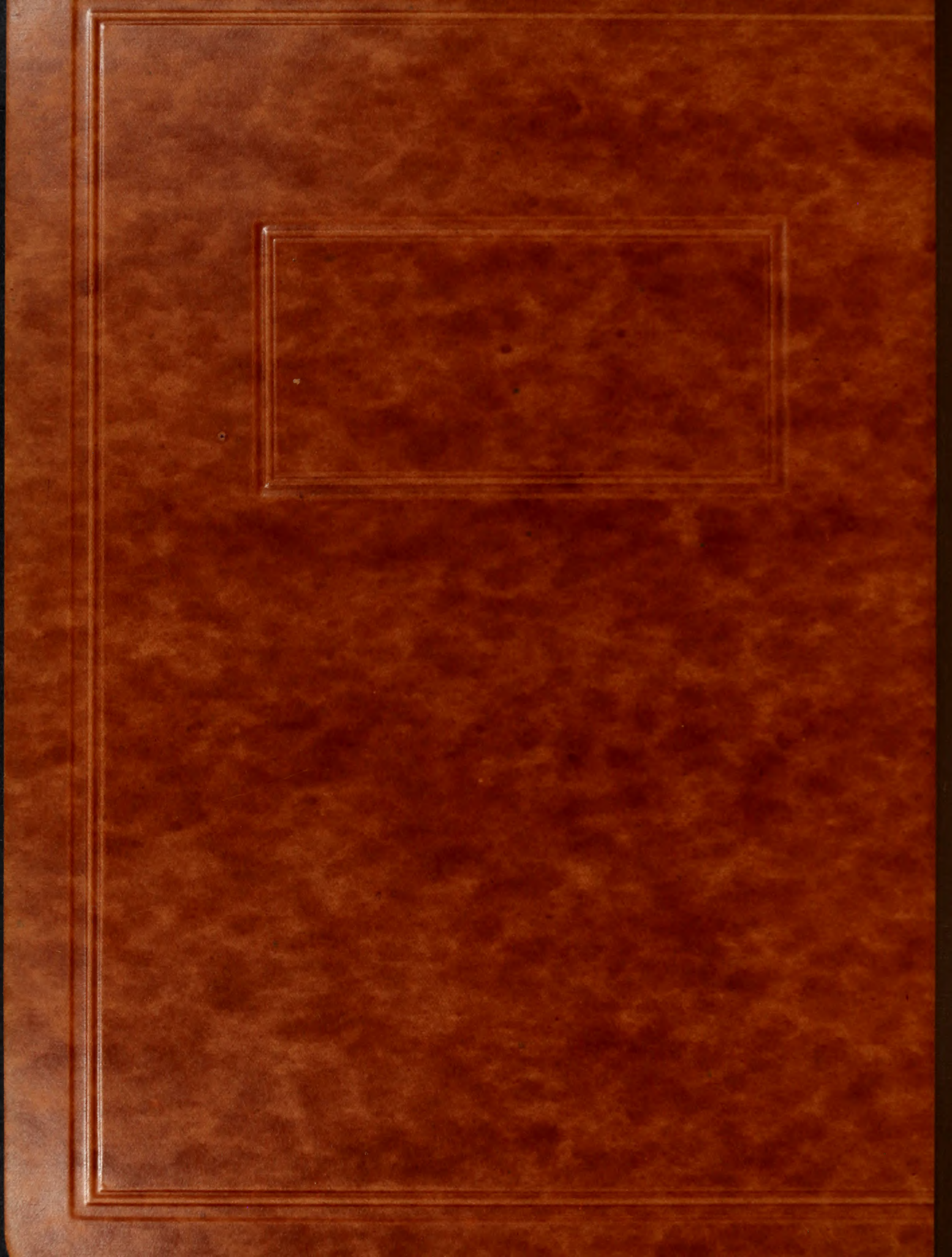


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BOSTON UNIVERSITY

GRADUATE SCHOOL

THESIS

META TOLUENE SULPHONIC ACID and RELATED COMPOUNDS

Submitted by

Charles Francis Hitchcock Allen

(A.B., Boston University, 1919)

In partial fulfilment of requirements for
the degree of Master of Arts

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DATA FOR THE SUBSTITUTION OF SUBSTITUTED COMPOUNDS

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META TOLUENE SULPHONIC ACID and RELATED COMPOUNDS

Theoretically toluene should yield three isomeric mono sulphonic acids, in which the entering sulphonic acid group occupies the positions ortho, meta, or para to the methyl group.

The action of sulphuric acid on toluene was first investigated by Jaworsky, (Ztschr. Chem. 1,272), who described one toluene sulphonic acid as the resulting compound. In 1869 Engelhardt and Latschinoff (Ibid. 617), heated toluene with sulphuric acid and made and studied the potassium salt of the resulting acid. They obtained two forms, and identified them by fusion with caustic potash which converted them into the ortho and para cresols, showing that sulphonation had taken place in the positions ortho and para to the methyl group.

Barth (Ann. chem. (Liebig) 152,91), working similarly but fusing under different conditions which also caused oxidation of the methyl group to a carboxyl group obtained para hydroxy benzoic acid and salicylic acid (ortho hydroxy benzoic acid.) This also proved that the sulphonic acid group had entered in the ortho and para positions.

Anna Wolkow (Ztschr. Chem (1870) 321), confirmed this work but ascribed the meta position to the sulphonic acid that passed into salicylic acid. She also made two acid chlorides and amides and recorded their melting points.

Fittig and Ramsay (Ann. chem. (Liebig) 168,242) studied this result of Anna Wolkow, and to determine and settle the constitutions of the sulphonic acids, carefully prepared and purified

META-TOLUENE SULPHONIC ACID AND RELATED COMPOUNDS

Theoretically toluene should yield three isomeric mono-sulphonic acids, in which the esterifying sulphonic acid group occupies the positions ortho, meta, or para to the methyl group. The action of sulphuric acid on toluene was first investigated by Jaksch (Bericht. Chem. 1, 275), who described one toluene sulphonic acid as the resulting compound. In 1838 Liebig and Lassaigne (Liebig, 81), heated toluene with sulphuric acid and water and obtained the potassium salt of the resulting acid. They obtained two forms, and identified them by fusion with caustic potash which converted them into the ortho and para isomers, showing that sulphonation had taken place in the positions ortho and para to the methyl group.

Burns (Ann. Chem. (Liebig) 153, 51), working similarly but under different conditions which also caused oxidation of the methyl group to a carboxyl group obtained para-hydroxy-benzoic acid and salicylic acid (ortho-hydroxy-benzoic acid). This also proved that the sulphonic acid group had entered in the ortho and para positions.

Anna Wolke (Bericht. Chem. (Liebig) 1870, 321), confirmed this work but ascribed the meta position to the sulphonic acid that passed into salicylic acid. She also made two acid chlorides and amides and recorded their melting points.

Wittig and Remy (Ann. Chem. (Liebig) 168, 343) studied this result of Anna Wolke, and to determine and settle the constitution of the sulphonic acids, carefully prepared and purified

their sulphonic acids; they proved definitely that no meta acid was formed, and that the products were only the ortho and para toluene sulphonic acids.

Hubner and Post (Ann. chem. (Liebig) 169,47) worked on pure para brom toluene, and obtained two para brom toluene mono-sulphonic acids, one of which they proved to be the ortho acid by removal of the bromine by metallic sodium, and oxidation to salicylic acid. By exclusion they decided that the other acid must be one containing the sulphonic acid group in meta position to the methyl group.

F.C.G. Müller (same as Hubner and Post) made the barium salt of ortho brom toluene sulphonic acid, and then removed the bromine by treatment with sodium amalgam. The excess of alkali was removed by sulphuric acid, the sodium sulphate removed by evaporation and crystallization, and the residue dried. On treatment with phosphorus pentachloride an oily toluene sulphonch chloride was obtained; this was decomposed by heating with water, the hydrochloric acid removed by repeated evaporations, and the syrup thus obtained evaporated to a crystalline condition. Several salts were made and studied. His amide melted at 90-91. Because this acid differed in properties from the two previously mentioned, Müller considered it to be the meta toluene sulphonic acid.

About this time F. Gervor (Ann. chem. (Liebig) 169,383), made ortho diazo toluene sulphonic acid by subjecting ortho toluidine sulphonic acid to nitrous fumes. This was decomposed

these sulphonic acids; they proved definitely that no meta acid was formed, and that the products were only the ortho and para toluene sulphonic acids.

Hopper and Post (Ann. Chem. (Liebig) 189, 47) worked on pure para toluene, and obtained two para toluene sulphonic acids, one of which they proved to be the ortho acid by removal of the bromine by metallic sodium, and oxidation to estroic acid. By examination they decided that the other acid must be one containing the sulphonic acid group in meta position to the methyl group.

F. G. G. Miller (same as Hopper and Post) made the meta acid of ortho toluene sulphonic acid, and then removed the bromine by treatment with sodium amalgam. The excess of amalgam was removed by sulphuric acid, the sodium sulphate removed by evaporation and crystallization, and the residue dried. On treatment with phosphorus pentachloride an oily toluene sulphonic acid was obtained; this was decomposed by heating with water, the phosphoric acid removed by repeated evaporations, and the crude toluene sulphonic acid evaporated to a crystalline solid. Several white crystals were obtained. His melting point was 30-32°. Because this acid differed in properties from the two previously mentioned, Miller considered it to be the meta toluene sulphonic acid.

About this time E. Gerver (Ann. Chem. (Liebig) 189, 388) made ortho diso toluene sulphonic acid by nitrating ortho toluene sulphonic acid to nitro toluene. This was decomposed

with alcohol under pressure, and a sodium salt of the acid obtained; this was converted into the chloride and an amide which melted at 148, differing in this and other properties from the amides of the ortho and para toluene sulphonic acids previously known.

In 1874 Pechmann (Ibid., 173,195) obtained a quantity of para toluidine meta sulphonic acid by heating para toluidine with sulphuric acid, and crystallizing out the para toluidine ortho sulphonic acid and disulphonic acids, leaving the meta acid in solution because of its greater solubility. The diazo compound was made by treatment of the acid in alcoholic suspension with nitrous fumes, and decomposed with alcohol under pressure. Various salts of the resulting sulphonic acid were made and studied, also the chloride and amide which melted "somewhere below 100".

In 1875 Pagel (Ann. chem. (Liebig) 176,297) working on ortho toluidine sulphonic acid, made a toluene sulphonic acid which resembled Muller's. His amide melted at 104.

In 1877 Beckurts (Ber.d.che. Ges. 10, 943), seeking for a good method of obtaining pure ortho toluene sulphonic acid, heated toluene and sulphuric acid in the ordinary way, and made the potassium salts of the resulting acids. By treatment with phosphorus pentachloride he obtained the acid chlorides which he separated by cooling to -15, and filtering off the solid para compound. The remaining liquid was transformed into an amide and purified by fractional crystallization. Two

compounds were obtained with sharp melting points of 153 and 104. From this work he concluded that the sulphonation of toluene yielded all the three possible acids.

Fahlberg (Am. Chem. J. 1, 170), doubted Beckurts' statement, because although his acid showed different properties he neglected to prove its constitution by converting it into the hydroxy benzoic acid. He therefore repeated Beckurts' work, and identified the amide melting at 154 as coming from ortho toluene sulphonic acid, by conversion into salicylic acid. The other amide with a sharp, constant melting point of 108 was oxidized, and the products separated and identified as para sulphamine benzoic acid, anhydro ortho sulphamine benzoic acid, and acid potassium ortho sulphobenzoate. These were the products one would expect from an oxidation of a mixture of the ortho and para toluene sulphonamides. Further proof that his acid was a mixture was obtained by mixing amounts of pure ortho and para toluene sulphonic acids, and by repeated crystallizations a form was obtained which melted at 108.

F.H.S. Muller (Ber. d. chem. Ges. 12, 1348), mentioned the formation of meta toluene sulphonic acid by the action of sulphurous acid upon the corresponding diazo compound, but gave no details except the melting points of his amide, anilide, and toluides.

Claesson and Wallin in 1879 (Ibid., p.1848), claimed that they had obtained meta toluene sulphonic acid by the action

compounds were obtained with sharp melting points of 133 and 104. From this work he concluded that the sulfonation of toluene yielded all the three possible acids.

Lehmann (Ann. Chem. 7, 1, 173), doubted Beckurts' statement, because although his acid showed different properties he neglected to prove its constitution by converting it into the hydroxy benzoic acid. He therefore repeated Beckurts' work, and identified the amide melting at 134 as coming from ortho toluene sulfonic acid, by conversion into salicylic acid. The other amide with a sharp, constant melting point of 108 was oxidized, and the products separated and identified as para sulfonamide benzoic acid, anhydrous ortho sulfonamide benzoic acid, and acid potassium ortho sulfonamide. These were the products one would expect from an oxidation of a mixture of the ortho and para toluene sulfonamides. Further proof that this acid was a mixture was obtained by mixing amounts of pure ortho and para toluene sulfonic acids, and by repeated crystallizations a form was obtained which melted at 103.

F.H.S. Miller (Ber. d. chem. Ges. 13, 1348), mentioned the formation of para toluene sulfonic acid by the action of sulphurous acid upon the corresponding diazo compound, but gave no details except the melting points of his amide, anhydride, and toluide.

Glasson and Wallin in 1875 (Ibid., p. 1886), claimed that they had obtained meta toluene sulfonic acid by the action

of chlorsulphonic acid upon toluene. They used very large quantities of materials. They obtained three acids, and identified them as the ortho and para, and called the third the meta acid, despite the fact that they had knowledge of Fahlberg's work.

The next step was undertaken by R. Otto (Ibid, 13, 1292), at the request of Beckurts. He examined some of the latter's supposed meta toluene sulphonamide, and found it to be a mixture of the amides of the ortho and para acids.

Neville and Winther (Ibid. 13, 1940), while investigating the formation of amino sulphonic acids, obtained a toluene sulphonic acid by heating ortho diazo toluene sulphonic acid with alcohol under pressure, and also by reducing brom toluene sulphonic acid with sodium amalgam. It was converted into the chloride and amide, - the latter melting at 106.5-107.5.

In 1886, Valin (Ibid. 2952), convinced by the work of Otto that Fahlberg's views were correct, and that he and Klason had not obtained meta toluene sulphonic acid, again attacked the problem; an acid was made and salts described.

In 1891, Metcalf (Am. Che. J. 15,301) (Dissertation, 1892), proved that decomposition of para diazo toluene meta sulphonic acid with ethyl alcohol under pressure resulted in the formation of para ethoxy meta toluene sulphonic acid in far greater quantity. Consequently the toluene meta sulphonic acid could not have been obtained by either Pechmann or Valin.

of chlorosulfonic acid upon toluene. They used very large quantities of materials. They obtained three acids, and identified them as the ortho and para, and called the third the meta acid, despite the fact that they had knowledge of Leibert's work.

The next step was undertaken by P. Otto (1914, 13, 1923), at the request of Geckeler. He examined some of the latter's supposed meta toluene sulfonic acids, and found it to be a mixture of the acids of the ortho and para acids. Neville and Winkler (1914, 13, 1919), while investigating the formation of toluene sulfonic acids, obtained a toluene sulfonic acid by heating ortho toluene sulfonic acid with alcohol under pressure, and also by reducing from toluene sulfonic acid with sodium amalgam. It was converted into the chloride and nitrate, - the latter melting at 105.5-107.5. In 1926, Vain (1926, 3353), convinced by the work of Otto that Leibert's views were correct, and that he had indeed had not obtained meta toluene sulfonic acid, again attacked the problem; an acid was made and salts described.

In 1921, Matsui (An. Org. 7, 19, 301) (1921), proved that decomposition of pure toluene acid with ethyl alcohol under pressure resulted in the formation of pure toluene sulfonic acid in far greater quantity. Consequently the toluene meta sulfonic acid could not have been obtained by either Geckeler or Vain.

Griffin, (Dissertation, 1895), prepared what he thought was a solution of the meta toluene sulphonic acid from the amide, and made and studied several salts as well as the anilide and toluides. However he did not investigate his solution to find out what it contained, but went ahead on the assumption that he had a solution of this acid. It is on the basis of his lack of investigation that I am working.

The derivatives of para toluene sulphonic acid have been made and studied by Newell, (Dissertation, 1895), and are being investigated further. He prepared para tolyl phenyl sulphone by the Friedal-Crafts reaction, para phenyl sulphone benzoic acid by oxidation of the sulphone with chromic acid, its salts, chloride, amide, and anilide, and para benzoyl diphenyl sulphone from the acid by the Friedal-Crafts reaction, and studied their reactions and properties.

The analogous derivatives of ortho toluene sulphonic acid were made and studied by Canter, (Dissertation, 1900). He prepared ortho tolyl phenyl sulphone by the Friedal-Crafts reaction, ortho phenyl sulphone benzoic acid by oxidation of the sulphone by potassium permanganate, its chloride, amide, and anilide, and ortho benzoyl diphenyl sulphone from the acid by the Friedal-Crafts reaction.

The analogous derivatives of the meta toluene sulphonic acid with one or two exceptions have not been made or studied, nor has the acid itself been prepared in a form which could be recognized. The following derivatives of meta toluene sulphonic acid have been made and studied; the amide by Müller, Pechmann,

Graftin (Dissertation, 1892), prepared what he thought was a solution of the meta-toluenesulphonic acid from the amide, and made and studied several salts as well as the amide and sulfide. However he did not investigate the solution to find out what it contained, but went ahead on the assumption that he had a solution of this acid. It is on the basis of his lack of investigation that I am working.

The derivatives of meta-toluenesulphonic acid have been made and studied by several (Dissertation, 1892), and are being investigated further. He prepared para-tolyl phenyl sulphone by the Friedel-Crafts reaction, para-phenyl sulphonic benzoic acid by oxidation of the sulphone with chromic acid, the salts, chlorides, amides, and anilides, and para-benzoyl diphenyl sulphone from the acid by the Friedel-Crafts reaction, and studied their reactions and properties.

The analogous derivatives of ortho-toluenesulphonic acid were made and studied by Gaster (Dissertation, 1900). He prepared ortho-tolyl phenyl sulphone by the Friedel-Crafts reaction, ortho-phenyl sulphonic benzoic acid by oxidation of the sulphone by potassium permanganate, the chlorides, amides, and anilides, and ortho-benzoyl diphenyl sulphone from the acid by the Friedel-Crafts reaction.

The analogous derivatives of the meta-toluenesulphonic acid with one or two exceptions have not been made or studied, nor has the acid itself been prepared in a form which could be recognized. The following derivatives of meta-toluenesulphonic acid have been made and studied: the salts by Miller, Beckmann,

The object of this paper is to prepare a volume of
 Pagel, Beckurts, F.H.S. Muller, Nevile and Winther, Chase
 Palmer, Klason, Valin, Noyes and Walker, Metcalf, and Griffin;
 meta sulphamine benzoic acid by Limpricht and Uslar, and Grif-
 fin; meta toluene sulphon anilide and toluidine by Muller and
 Wiesinger, (Ber. d. chem. Ges, 12,1348), and by Griffin; the
 latter also made and studied several metallic salts.

The literature on the ortho and para toluene sul-
 phonic acids and their derivatives is voluminous, and covers
 a great many derivatives which have been thoroughly studied
 and whose structure has been determined. The literature on
 meta toluene sulphonic acid is very meagre, comparatively, and
 all that could be found is mentioned in this paper. This
 would seem to indicate that investigators have avoided this
 series, and apparently the reason is due to the difficulties
 encountered in isolating the free acid.

Page, Beckwith, F.E.S. Miller, Keville and Winkler, Chase, Palmer, Kline, Vain, Koye and Walker, Metcalf, and Griffin; also aliphatic ketones and alcohols by Winkler and Miller, and Griffin; also ketones and alcohols by Miller and Winkler; (Ber. 4. Chem. Ges. 18, 1898), and by Griffin; the latter also made and studied several ketone series.

The literature on the ether and para ketone aliphatic ketones and their derivatives is voluminous, and covers a great many derivatives which have been thoroughly studied and whose structure has been determined. The literature on ether ketone aliphatic ketone is very meagre, comparatively, and all that could be found is mentioned in this paper. This would seem to indicate that investigators have avoided this series, and apparently the reason is due to the difficulties encountered in isolating the free acid.

THEORETICAL DISCUSSION

The object of this paper is to prepare a solution of meta toluene sulphonic acid, as probably obtained by Griffin, by the most promising of the investigated methods and to find an acceptable one for isolating the acid in the solid state. After a solution is obtained similar to that found by Griffin, (loc. cit.), the intention is to remove as much water as possible by distillation under diminished pressure and then to precipitate the acid by the method of Kastle, (Amer. Chem. J., Vol.44, page 483), namely saturate the remaining solution with gaseous hydrochloric acid. It is hoped that in this way the solid acid may be obtained which can then be studied.

As has been proved by previous experimenters and discussed above, no direct method of sulphonating toluene will give any of the meta sulphonic acid. Therefore to get a compound containing a methyl group with a sulphonic acid group in the position meta to it some compound with these already in that position and containing some other group which can be replaced by hydrogen might be used, i.e., a disubstituted toluene. The two groups which can be readily replaced by hydrogen are the amino group and bromine, the former by the diazo reaction and the latter by treatment with metallic sodium; the easier of the two to prepare and replace is the amino group and this is the one made use of in this synthesis. This replacement has been widely studied (Amer. Chem. J., by Palmer 8, 243; Orndorff 9, 387; Graham 11, 319; Dashiell 15, 124; Metcalf 15, 301; Parks 15, 320; Shober 15, 379; Beeson 16, 244; and Dissertations by

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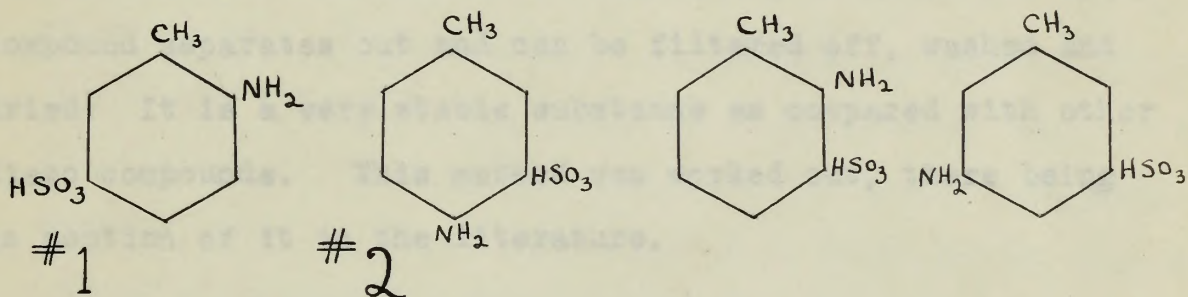
As has been proved by previous experiments and discussed above, no direct method of sulphonating toluene will give any of the meta-sulphonic acid. Therefore to get a compound containing a methyl group with a sulphonic acid group in the position meta to it some compound with these already in that position and containing some other group which can be replaced by hydrogen might be used, i.e., a disubstituted toluene. The two groups which can be readily replaced by hydrogen are the amino group and bromine, the former by the direct reaction and the latter by treatment with metallic sodium; the easier of the two to prepare and replace is the amino group and this is the one made use of in this synthesis. This replacement has been widely studied (Amer. Chem. J., by Palmer 6, 343; Orndorff 6, 387; Graham 11, 319; Washell 15, 134; Metcalf 15, 301; Parks 15, 330; Grover 15, 373; Benson 15, 344, and Dissertation by

Weida, Cameron, and Chamberlain, all 1894.), and the various conditions affecting it determined. The foregoing investigators decomposed their diazo compounds with alcohols sometimes using certain substances to cause the alkoxy or hydrogen reactions to take place. Later investigators (Buchka, *Berichte* 23, 1628, *St. Von Niemantowski, Ibid.*, 34, 3325 (1901), Ullman and Bieleck, *Ibid.*, 34, 2174, and Bigelow, *J. Amer. Chem. Soc.*, Vol. 41, 1566), have shown that this decomposition is greatly increased by the presence of copper powder. As the first method has been more extensively studied it was adopted in this case.

The action of methyl, ethyl, and n-propyl alcohols on diazo compounds has been well studied by the above authors, and it has been shown that the first two at ordinary pressures give the alkoxy reaction either in whole or in part; n-propyl alcohol gives the hydrogen reaction only. Also the first two give the hydrogen reaction in the presence of zinc dust or sodium carbonate, but in these cases form salts of the acid. On account of its rarity n-propyl alcohol was not used, but n-butyl alcohol which is available in large quantities and in a pure condition was employed. Recent advances in fermentation as applied to organic chemistry have made this substance easily obtainable as a byproduct in the production of acetone which was needed in large amounts during the late war. Its use was found to be successful; it boils at 117 and so can be easily distilled off after decomposition has been effected without a great increase in temperature above the boiling point of water, which increase

Griffin (loc. cit.) showed to cause carbonization. For this reason i-amyl alcohol although available was not considered,-- also higher alcohols because of this fact and because of their rarity.

Of the four amino toluene sulphonic acids theoretically possible in which the sulphonic acid group is in the meta position in reference to the methyl group only two are commonly known, No. 1, and No. 2.

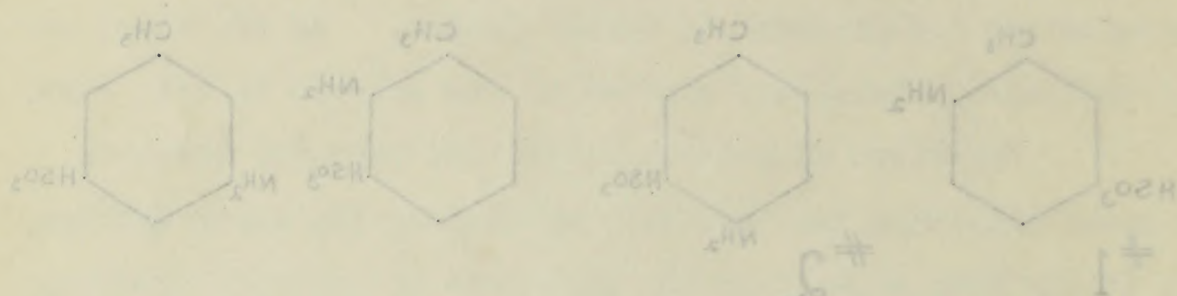


Methods of preparing No. 1 and No. 2 were found but without details, so a method had to be worked out to obtain them easily and in good yield. After a little experimenting No. 1, or ortho toluidine sulphonic acid was readily obtained in good yield and in a fairly pure condition. No. 2, or para toluidine meta sulphonic acid was obtained in only a ten per cent yield and by means of a much more difficult method of procedure. The preparation of this acid was undertaken first and consumed a long time; Griffin did his work starting with this acid and I hoped to get as far as he did earlier. It was then available in the market as was the ortho toluidine sulphonic acid, but now neither are available.

The methods employed by earlier investigators when they wished to isolate their diazo compounds was to suspend the

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The methods employed by earlier investigators when they wished to isolate their diazo compounds was to suspend the

substance to be diazotized in alcohol, and then pass in nitrous fumes generated by dropping concentrated nitric acid onto arsenious oxide. The diazo compound from ortho toluidine sulphonic acid is so nearly insoluble in water that it was found possible to diazotize it in water suspension, and generate the nitrous fumes in the solution itself by adding a solution of sodium nitrite to the water suspension containing hydrochloric acid. After a short time the diazo compound separates out and can be filtered off, washed and dried. It is a very stable substance as compared with other diazo compounds. This method was worked out, there being no mention of it in the literature.

substance to be dissolved in alcohol, and then pass in nitrogen fumes generated by dropping concentrated nitric acid onto potassium oxide. The glass compound from the solidifying substance will be as nearly insoluble in water as it was found possible to dissolve it in water separation, and generate the nitrogen fumes in the solution itself by adding a solution of sodium nitrite to the water suspension containing hydrochloric acid. After a short time the glass compound separates out and can be filtered off, washed and dried. It is a very stable substance as compared with other glass compounds. This method was worked out, there being no mention of it in the literature.

SULPHONATION OF ORTHO TOLUIDINE

Of the possible sulphonic acids of ortho toluidine the commercial product of former days was the one in which the sulphonic acid group was in the para position to the amine group, and meta to the methyl group; thus this acid could find use in preparing the toluene meta sulphonic acid if a method of replacing the amino group by hydrogen could be found. This acid is not now on the market in America because of its limited use in dyestuffs. It is mentioned in Schultz and Julius, ("Farbestoff Tabellen", 1894 Edition, Trans. by F. C. Green), Cain, ("The Manufacture of Intermediate Products for Dyes") and Nevile and Winther, (Ber. d. chem. Ges. 13, 1940.), which latter give a method of preparation which was used industrially, -the baking of ortho toluidine sulphate. Their description is rather indefinite but after a few preliminary trials a suitable method was found. I will describe all the experiments attempted, and include the one finally adopted. The ortho toluidine used was obtained from Eastman Kodak Co., (Practical.)

Experiment 1.

Ortho toluidine was suspended in water and conc. sulphuric acid added with vigorous stirring until all the amine had dissolved. The solution was heated to boiling until the sulphate had dissolved, and then cooled and the crystals thus obtained filtered off and dried. This was then powdered and ground with some powdered oxalic acid. These mixtures with and without oxalic acid were then baked until a sample was completely soluble in sodium hydroxide. The mass had become a deep grayish purple. It dis-

SUBSTITUTION OF OTHER TOXICITY

Of the possible substituents of the following
the compound of interest of former days was the one in which the
substituent with group was in the same position as the main
group, and also in the same group. This would be the
use in preparing the following with a method of
replacing the main group of hydrogen with a group. This would
be not on the basis of the reaction because of the reaction use
is possible. It is mentioned in Goss and Goss, ("The
Tobacco", 1924 Edition, 2nd ed. by E. G. Goss, Goss, ("The
Manufacture of Intermediate Products for Pipes") and Davis and
Winters, (Ser. 2, 1925, Dec. 15, 1925), which latter give a
method of preparation which was used industrially, the basis of
other substituents. Their description is rather indefinite
but after a few preliminary trials a suitable method was found.
I will describe all the experiments attempted, and include the
one finally adopted. The other substituents were obtained from
Eastman Kodak Co., (Trenton, N.J.)

Experiment I.

Ortho-substituted was suspended in water and conc. sul-
phuric acid added with vigorous stirring until all the main had
dissolved. The solution was heated to boiling until the substituents
had dissolved, and then cooled and the crystals thus obtained fil-
tered off and dried. This was then powdered and ground with some
powdered oxalic acid. These mixtures with and without oxalic
acid were then baked until a sample was completely soluble in
sodium hydroxide. The mass had become a deep yellow color. It is

solved in water to give a deep red solution. Nothing satisfactory was obtained from any of these bakes, the formation of a red dyestuff as mentioned by Neville and Winther seeming to be formed in a great quantity and very easily. Hence this method was discarded.

Experiment 2.

In this case an excess of sulphuric acid was used. After the oxalic acid had all been decomposed or driven off the mass turned black and became very pitchy. Nothing could be done with it so it was thrown away.

Experiment 3.

In this case an excess of ortho toluidine was used. The red dyestuff was formed in great amount and very easily. The temperature was kept below 195 to lose none of the toluidine which boiled at 199.

Experiment 4.

This method gave the best results and is the one employed in the preparation of all the material used in the thesis. Equal weights of ortho toluidine and sulphuric acid (100gms. of each were used; 100gms. of ortho toluidine is 108cc., and 100gms. of sulphuric acid (s. g. 1.84) are 56cc.), were mixed and baked at 190-195 until a sample would dissolve in ten per cent sodium hydroxide solution to give a clear solution; this took one and a half hours. The mixture at first melts in the solution of the sulphate and sulphuric acid formed by the heat of combination; as heating is continued it gradually becomes solid and finally very hard; it has become gray in color. When it is perfectly

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dry a test is made to see if it dissolves in sodium hydroxide giving a clear solution. If so, sulphonation is complete. By using an oven with a glass door the reaction mixture can be watched and the completion of the baking observed. However the test for complete solubility should always be made. The addition of powdered oxalic acid to the reaction mixture did not seem to be of advantage, because no visible reaction commenced until this had been driven off or decomposed. It is usually added in producing sulphonic acids by baking the sulphates of the amines to increase the porosity of the mass and thus facilitate removal of the product. However here the only effect seemed to be to retard the reaction, as the product was the same hard grayish mass as without the acid, and it was just as difficult to dig it out. It took an hour longer to complete the reaction with the addition of the oxalic acid.

The best results were obtained when the temperature of the oven was kept at 193, although five degrees variation did not appreciably affect the product. A lower temperature gives little or no action, while a higher one drives off the ortho toluidine and also seems to favor the formation of the red dyestuff.

As stated above, complete sulphonation is shown by the solubility of the acid in ten per cent sodium hydroxide solution. If any unchanged amine is present as sulphate the solution will become milky due to liberation of the insoluble amine. On boiling a solution of the acid a slight hydrolysis takes place so that the smell of ortho toluidine is present,

... a test is made to see if it dissolves in sodium hydroxide
giving a clear solution. If no solution is obtained, by
adding an even with a glass stopper and reaction mixture can be
watched and the completion of the taking observed. However
the test for complete solubility should always be made. The
addition of powdered chalk to the reaction mixture will
not seem to be of advantage, because no visible reaction can
be seen until it has been driven off or decomposed. It is
usually added in increasing amounts until by taking the uni-
phases of the mixture to increase the porosity of the mass and
thus facilitate removal of the product. However here the
only effect seemed to be to retard the reaction, as the product
was the same hard grayish mass as without the solid, and it was
just as difficult to dig it out. It took an hour longer to
complete the reaction with the addition of the chalk solid.
The best results were obtained when the temperature
of the oven was kept at 185, although five degree variation
did not apparently affect the product. A lower temperature
gives little or no action, while a higher one drives off the
ortho compound and also seems to favor the formation of the
para product.
As stated above, complete solubility is shown by
the solubility of the solid in the pure sodium hydroxide
solution. If any unchanged alkali is present as impurity the
solution will become sticky due to liberation of the insoluble
alkali. On boiling a solution of the solid in dilute hydrochloric
acid it was found that the small amount of ortho compound is present.

yet the solution is always perfectly clear.

The product or "bake" appears as a hard grayish mass, slightly porous. It is dug out, pulverized, boiled up in a large evaporating dish, containing water and a little (10cc.) hydrochloric acid, with animal charcoal and filtered. The solution should be almost colorless. The effect of the slight amount of hydrochloric acid was accidental; the first solutions were always a deep red color due to some of the red dyestuff seeming to be present, and the longer the solution was boiled the redder it got. A little acid seems to prevent this entirely. The solution is evaporated on a water bath until a scum has formed on the surface when it is allowed to cool and crystallize. It crystallizes in small almost white needles, which appear to fill the entire liquid; this is deceptive as on filtering the bulk is considerably reduced. They fall to a powder when they are dry. If they are colored red or pink they are washed while still on the filter with water; alcohol does not remove this color.

The acid as formed has no melting point, but chars and decomposes on heating. A sample was tested for nitrogen and sulphur with very good positive results. On fusion with caustic soda and acidification of the product a positive reaction was obtained on the addition of bromine water as is customary with phenols.

It was identified as identical with the acid of Nevile and Winther (loc. cit.) by conversion thru the diazo compound into dinitro ortho cresol, melting at 85.8 as described under the description of the diazo compound.

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soda and addition of the product a positive reaction was ob-

tained on the addition of bromine water as is customary with

phenols.

It was identified as identical with the acid of Neville

and Winter (loc. cit.) by comparison with the same compound

into dihydro-ortho-cresol, melting at 88.5 as described under

the description of the same compound.

SULPHONATION OF PARA TOLUIDINE

Metcalf, (loc. cit.), gives a method for the preparation of the sulphonic acids of para toluidine, and states that both the possible acids are formed, with the meta position (referred to the methyl group) in good yield. Schultz and Julius, ("Farbestoff Tabellen", 1894 Edition, Trans. by F. C. Green), and Neville and Winther, (loc. cit.), say that the sulphonation of para toluidine gives a mixture of the sulphonic acids, with the ortho (referred to the methyl group) sulphonic acid in a much greater yield. As the sulphonation of para nitro toluene gives (Dissertation, R. S. Norris, BPL. 5976.109) a ninety-five per cent yield of the ortho sulphonic acid, it would seem as though the amino compound should give a large yield of the acid (sulphonic acid group ortho to the methyl group,) and such was found to be the case.

I followed Metcalf's directions as follows: in an apparatus fitted with an automatic stirrer and a thermometer I placed 200 grams (110cc.) of twenty per cent fuming sulphuric acid. I then slowly added with rapid stirring 100grams of powdered para toluidine which was obtained from the Newport Chemical Works. The addition took thirteen minutes. The initial temperature of the solution was 18°C. The maximum was obtained when about half the toluidine had been added and was 148°C. The final temperature was 130°C. After addition was complete I stirred for five minutes, and then slowly heated the mixture to 180°C. and kept it there for an hour. Sulphona-

tion was then complete. I then poured it into an equal volume of cold water (220cc.) in an evaporating dish and allowed it to stand over night. The next day the dish seemed filled with grayish crystals; these were filtered off. The solution was allowed to stand for four weeks with no results. (Metcalf says that the disulphonic acid separated in three weeks from his solution.)

I dissolved the crude acid obtained as above in ten liters of water (Metcalf's directions) and precipitated the excess of sulphuric acid with barium hydroxide, and then filtered the solution. It was a clear brownish color. I then evaporated to 100cc. A smell of para toluidine was always present in the vapor indicating a probable hydrolysis of the acid. (Nevile and Winther (loc. cit.) say that this sulphonic acid can be hydrolyzed by heating with water). A test after sulphonation and before evaporation showed a sample to be completely soluble in water, and no cloudiness was produced when a sample was dissolved in sodium hydroxide, as is the case if a solution of para toluidine sulphate is dissolved in the same reagent. When the volume had reached 100cc. a light brown crust had formed on top of the liquid and on cooling and filtering two products were obtained; a light brown powdery substance in larger amount (47.5 grams.), and a small amount of hard square brown crystals. On evaporating the filtrate nearly to dryness more material separated which did not look like either of the above substances; it weighed twenty grams. This has not been investigated as yet.

This was then completed. I then poured it into an equal
 volume of cold water (250cc.) in an evaporating dish and al-
 lowed it to stand over night. The next day the dish seemed
 filled with grayish crystals, these were filtered off. The
 solution was allowed to stand for four weeks with no result.
 (Mitschke says that the aliphatic acid separated in three
 weeks from his solution.)
 I dissolved the crude acid obtained as above in ten
 liters of water (Mitschke's directions) and precipitated the
 excess of aliphatic acid with sodium hydroxide, and then fil-
 tered the solution. It was a clear brownish color. I then
 evaporated to 100cc. A small amount of water was always
 present in the vessel containing a probable hydrolysis of the
 acid. (Giville and Winter (loc. cit.) say that this al-
 iphatic acid can be hydrolyzed by heating with water). A test
 after saponification and before evaporation showed a sample to
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 the same reagent. When the volume had reached 100cc. a light
 brown crust had formed on top of the liquid and on cooling and
 filtering two products were obtained; a light brown powdery
 substance in larger amount (47.5 grams), and a small amount
 of hard opaque brown crystals. On evaporating the filtrate
 nearly to dryness more material separated which did not look
 like either of the above substances; it weighed twenty grams.
 This has not been investigated as yet.

As the brownish powdery substance was mixed with the flat crystals produced above a method had to be found to separate them and purify each. I screened them as much as possible with good results. I removed the last of the fine powder by dissolving it off with hot water. Metcalf said that they could be separated by their difference in specific gravity in fifty per cent alcohol but this method was unsuccessful. I boiled up the aqueous solution of the powdery substance with animal charcoal, filtered and evaporated to crystallization. Square, flat, white crystals were obtained identical in all but color with those mentioned above. They are soluble with difficulty in cold water, readily in hot, and insoluble in alcohol. In these properties and in appearance they compare to the ortho sulphonic acid of para toluidine as made and described by Parks, (Dissertation, 1892). Metcalf and Nevile and Winther say that the meta sulphonic acid of para toluidine forms needles, but I obtained nothing that could in any way be called needles. This sulphonic acid had no melting point, but charred and decomposed. A test for elements showed nitrogen and sulphur to be present. The aqueous solution had a strong acid reaction to litmus.

In order to see if this might be the desired acid I tried to prepare an acid chloride with phosphorus pentachloride in the usual way, and then intended to convert it into the amide and get a melting point for identification. I used equal weights of the acid and phosphorus pentachloride. I ground them together at ordinary temperature in a mortar: no result. I heated it on

a water bath: no result. I heated it on a gauze over a flame: no result except decomposition and carbonization. However I poured water into the mixture and decomposed the excess of phosphorus pentachloride, and filtered. A gummy brownish mass remained which was insoluble in all reagents tried, (methyl and ethyl alcohol, benzine, petroleum ether, (40-60), water, carbon tetrachloride, dilute hydrochloric acid, acetone, and acetic acid.) Ethyl ether extracted a very small amount, just enough to color it yellow, and leave a yellow color on porcelain on evaporation, but not enough to make a study of the properties. On shaking up with concentrated ammonia the mass became very finely divided, but no solution appeared to take place; on filtering and evaporating to dryness there was no residue.

The material mentioned above as being the final product from the sulphonation of para toluidine, obtained in a yield of twenty grams or ten per cent yield and then uninvestigated, has since been identified as the acid I was looking for, or para toluidine meta sulphonic acid. A small amount was cooled and diazotized in the usual manner; the diazo compound seemed to be insoluble in the amount of water used, for a white crystalline needle-like precipitate appeared. This was decomposed by boiling with dilute nitric acid (Nevile and Winther, loc. cit.), and on cooling small tufts of yellow needles separated. These were filtered off and dried, then recrystallized from alcohol. The best portions of these were then recrystallized from ether and the melting point determined.

They melted at 79.5-79.8 (uncorr.) Nevile and Winther gave 79-80, showing that they did not purify their compound. The product is dinitro para cresol, or 3-nitro, 4-hydroxy, 5-nitro toluene.

Experiment 1.

I suspended some ortho toluene sulphonic acid in denatured alcohol, and passed it a rapid current of nitrous fumes, generated by dropping concentrated nitric acid into a saturated solution of sodium nitrite, for fifteen minutes. The suspension became slightly warm, and rather pasty at the end. I allowed it to stand a hour, and at the end of that time it had become very thick and pasty. I then filtered it off by suction, washed with ether, and dried.

Experiment 2.

The procedure used was the same as above using ethyl alcohol in place of denatured alcohol, but for some reason no dinitro product appeared to take place. The acid was filtered off and used again.

Experiment 3.

A saturated water solution of the acid was made by boiling some of it up with water, cooling and filtering. No precipitate appeared on passing in nitrous fumes.

Experiment 4.

Some of the acid was dissolved in sodium carbonate solution, sodium nitrite solution added, and after

These results at 72.5-73.5 (uncert.) are the same as those given by the 72-73, showing that they did not really differ. The product is identical with that of 7-nitro, 4-hydroxy, 5-nitro
nitro.

DIAZOTIZATION OF ORTHO TOLUIDINE SULPHONIC ACID.

Nevile and Winther (loc. cit.), stated that they obtained a diazo compound from their ortho toluidine sulphonic acid and described a few properties, but gave no details of manipulation, so I made several trials to determine the best acceptable method.

Experiment 1.

I suspended some ortho toluidine sulphonic acid in denatured alcohol, and passed in a rapid current of nitrous fumes, generated by dropping concentrated nitric acid into a saturated solution of sodium nitrite, for fifteen minutes. The suspension became slightly warm, and rather pasty at the end. I allowed it to stand a half hour, and at the end of that time it had become very thick and pasty. I then filtered it off by suction, washed with ether, and dried.

Experiment 2.

The procedure used was the same as above using ethyl alcohol in place of denatured alcohol, but for some reason no diazotization appeared to take place. The acid was filtered off and used again.

Experiment 3.

A saturated water solution of the acid was made by boiling some of it up with water, cooling and filtering. No precipitate appeared on passing in nitrous fumes.

Experiment 4.

Some of the acid was dissolved in sodium carbonate solution, sodium nitrite solution added, and after

cooling, concentrated hydrochloric acid added drop by drop. Nitrous fumes were given off, but no precipitate appeared.

Experiment 5.

This seems to be the best method and the one employed hereafter in the preparation of all the material subsequently used. The solid ortho toluidine sulphonic acid is suspended in concentrated hydrochloric acid and vigorously stirred. The solution becomes warm and the crystals change in appearance, probably due to the formation of the hydrochloride. The mass is then cooled to 5° , and sodium nitrite solution added slowly with stirring. Immediate reaction takes place, and the mass becomes very pasty as in the first experiment. After obtaining a reaction with starch iodide paper the mixture was allowed to stand a half hour, then filtered by suction, washed with ether and dried. In appearance it was identical with the diazo compound obtained in experiment 1, and can be kept in the same way.

That it was a diazo compound was shown as follows:

It was spotted on a piece of filter paper with an alkaline solution of H acid--a red coloration indicates the formation of a red azo dyestuff.

Some of the diazo compound was boiled with dilute nitric acid as described by Nevile and Winther, and a yellowish precipitate of needles obtained, which on recrystallization from denatured alcohol gave light yellow needles of dinitro ortho cresol, (2-hydroxy 3,5-dinitro toluene), melting at $82.5-84^{\circ}$ uncorr. (Nevile and Winther gave 85° for the pure substance.) This dinitro compound was obtained in nearly quantitative yield

cooling, concentrated hydrochloric acid added drop by drop. Nitrous fumes were given off, but no precipitate appeared.

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This seems to be the best method and the one employed hereafter in the preparation of all the materials subsequently used. The solid ortho toluidine sulphonic acid is suspended in concentrated hydrochloric acid and vigorously stirred. The solution becomes warm and the crystals change in appearance, probably due to the formation of the hydrochloride. The mass is then cooled to 5° , and sodium nitrite solution added slowly with stirring. Immediate reaction takes place, and the mass becomes very heavy as in the first experiment. After obtaining a reaction with starch iodide paper the mixture was allowed to stand a half hour, then filtered by suction, washed with water and dried. In appearance it was identical with the diazo compound obtained in experiment 1, and can be kept in the same way.

That it was a diazo compound was shown as follows:

It was spotted on a piece of filter paper with an alkaline solution of H acid--a red coloration indicates the formation of a red azo dye.

Some of the diazo compound was boiled with dilute nitric acid as described by Neville and Wintner, and a yellowish precipitate of needles obtained, which on recrystallization from concentrated alcohol gave light yellow needles of dihydro ortho toluidine (3-hydroxy 3,5-dinitro toluene), melting at $88.5-89^{\circ}$ (Neville and Wintner gave 85° for the pure substance.) This dihydro compound was obtained in nearly quantitative yield.

indicating that the diazo compound was presumably pure.

PHYSICAL PROPERTIES OF THE DIAZO COMPOUND

It is almost insoluble in water, and is insoluble in denatured alcohol and ether.

It is a white solid which can be dried and kept without apparent decomposition; it gradually turns pink when exposed to the light for several days, so is kept in a brown bottle if not required for immediate use. It does not explode when struck with a hammer, but deflagrates violently if a flame is brought near or if heated on porcelain.

indicating that the glass compound was presumably pure.

PHYSICAL PROPERTIES OF THE GLASS COMPOUND

It is almost insoluble in water, and is insoluble

in benzene, alcohol and ether.

It is a white solid which can be dried and kept without apparent decomposition; it gradually turns pink when exposed to the light for several days, so is kept in a brown bottle if not required for immediate use. It does not explode when struck with a hammer, but detonates violently if a flame is brought near or it heated on porcelain.

DECOMPOSITION OF THE DIAZO COMPOUND

(1) With n-Butyl alcohol in the presence of sodium carbonate.

A portion of the dry diazo compound was placed in a flask connected with a reflux condenser, and solid sodium carbonate and n-butyl alcohol added. No reaction took place at ordinary temperature so heat was applied. Decomposition started at 65° and evolution of hydrogen proceeded evenly and smoothly until all the diazo compound had disappeared. The alcohol, at first colorless, became an orange and finally a brown color. The solution was then refluxed an hour to ensure complete decomposition of the diazo compound. The smell of an aldehyde was evident indicating that the hydrogen reaction was taking place; the solution was tested with Schiff's reagent and with ammoniacal silver nitrate with distinct positive results in both cases, showing aldehyde was present. The alcoholic solution was filtered from the sodium carbonate remaining, and the alcohol distilled off on an oil bath. A yellowish-orange porous solid was left in such a small amount that no derivatives could be made and studied. It was free from the diazo compound, shown by its giving no color with an alkaline solution of H acid.

(2) With n-Butyl Alcohol alone.

The previous experiment showed that n-butyl alcohol would decompose the diazo compound in the presence of sodium carbonate and replace the amino group by hydrogen, so this time a decomposition with the alcohol alone was tried. Decomposition took place evenly and smoothly as before at the same temperature, and the solution became a clear brownish-orange. Aldehyde was given off and tested for as before with positive results. The

DECOMPOSITION OF THE DIASO COMPOUND

(1) With *n*-Butyl alcohol in the presence of sodium carbonate. A portion of the dry diazo compound was placed in a flask connected with a reflux condenser, and solid sodium carbonate and *n*-butyl alcohol added. No reaction took place at ordinary temperature so heat was applied. Decomposition started at 85° and evolution of hydrogen proceeded evenly and smoothly until all the diazo compound had disappeared. The alcohol, at first colorless, became an orange and finally a brown color. The solution was then refluxed an hour to ensure complete decomposition of the diazo compound. The smell of an aldehyde was evident indicating that the hydrogen reaction was taking place; the solution was tested with Schiff's reagent and with ammoniacal silver nitrate with distinct positive results in both cases, showing aldehyde was present. The alcoholic solution was filtered from the sodium carbonate remaining, and the alcohol distilled off on an oil bath. A yellowish-orange porous solid was left in which a small amount of no derivatives could be seen and studied. It was free from the diazo compound, shown by its giving no color with an alkaline solution of H acid.

(2) With *n*-Butyl Alcohol alone.

The previous experiment showed that *n*-butyl alcohol would decompose the diazo compound in the presence of sodium carbonate and replace the active group by hydrogen, so this time a decomposition with the alcohol alone was tried. Decomposition took place evenly and smoothly as before at the same temperature, and the solution became a clear brownish-orange. Aldehyde was given off and tested for as before with positive results. The

alcohol was removed by distillation and a thick brownish syrupy liquid was left. This was easily soluble in water, so was dissolved, filtered, and the solution used in the following experiments. At this point it is similar in every way to the solution obtained by Griffin (loc. cit.) from the diazo compound of para toluidine meta sulphonic acid.

Subsequent preparations of this syrup were made in the above way with similar results in every case. The only precaution to be observed is that no part of the flask containing the reaction mixture be allowed to become too hot as the diazo compound is then decomposed violently leaving a grayish ash.

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grayish ash.

A STUDY OF THE SOLUTION OBTAINED BY THE DECOMPOSITION
OF THE DIAZO COMPOUND

The syrup which remained after distilling off the n-butyl alcohol was a thick brown viscous fluid in all cases. It has an acid reaction and is completely soluble in water. On testing it showed the presence of sulphur in quantity and the absence of nitrogen. Some was dissolved in water, filtered, and evaporated on the water bath. After its volume had been considerably reduced it turned a very dark brown, then blackish, and smelled very tarry. It did not crystallize at all, finally becoming very black. To a drop on a watch glass a drop and then an excess of concentrated hydrochloric acid was added but with no apparent result.

Another portion of the syrup was dissolved in water, boiled with purified animal charcoal, and filtered. The filtrate was colorless. It was then evaporated on the water bath and solidified completely. Some of this solid was ignited and a white ash was left; had it been a sulphonic acid there would have been no residue. A qualitative analysis of the ash was made and much phosphate and calcium found present; therefore this solid was presumed to be a mixture of calcium phosphate from the animal charcoal and perhaps the calcium salt of the sulphonic acid. This showed that animal charcoal could not be used for purposes of purification.

"Activated charcoal" has been advocated for decolorizing solutions as well as for absorbing toxic gases;

A STUDY OF THE SOLUTION OBTAINED BY THE DECOMPOSITION OF THE BINARY COMPOUND

The group which remained after distilling off the n-butyl alcohol was a thick brown viscous liquid in all cases. It has an acid reaction and is completely soluble in water. On testing it showed the presence of sulphur in quantity and the absence of nitrogen. Some was dissolved in water, filtered, and evaporated on the water bath. After the volume had been considerably reduced it turned a very dark brown, then blackish, and solidified very hard. It did not crystallize at all, finally becoming very black. To drop on a watch glass a drop and when an excess of concentrated hydrochloric acid was added but also no apparent result. Another portion of the group was dissolved in water, boiled with purified animal charcoal, and filtered. The filtrate was colorless. It was then evaporated on the water bath and solidified completely. Some of this solid was ignited and a white ash was left; had it been a sulphuric acid there would have been no residue. A qualitative analysis of the ash was made and much phosphate and calcium found present; therefore this solid was presumed to be a mixture of calcium phosphate with the animal charcoal and perhaps the calcium salt of the sulphuric acid. This showed that animal charcoal could not be used for purpose of purification.

"Activated charcoal" has been suggested for the colorless solutions as well as for removing toxic gases.

the author had become acquainted with this material while in the Chemical Warfare Service, and had obtained small samples of "Dorsite" and "Carbonite". Some of this was powdered and the brown solution boiled with it until most of the color was removed. The solution was then filtered and evaporated on the water bath; a white crystalline solid was again left. Investigation of the activated charcoal showed that concentrated acids extracted some substance which was thrown down in a flocculent white precipitate on making alkaline with ammonia. Therefore another sample of the activated charcoal was boiled with concentrated nitric acid, filtered, and the charcoal washed free from acid; this sample did not decolorize well.

A sample of a specially prepared charcoal for decolorizing purposes manufactured by the Barneby-Cheney Co. was obtained and tried, but was unsuccessful; the color was not removed.

Infusorial earth, kiesel guhr, and "Sil-o-cel" were also tried unsuccessfully; Fullers Earth made a very clear solution but no color was removed.

Some of the brown viscous solution was dissolved in water, the solution filtered and evaporated to a constant volume (estimated when no more vapor could be seen to condense) under diminished pressure (water pump) until it became more brown. It was then allowed to cool, and dry hydrochloric acid gas passed in, first to expel all air or other vapor

The water had become saturated with this material while in the Federal Water Service, and had appeared small amount of "hydrate" and "carbonate". Some of this was removed and the water collected before it was filtered of the color was removed. The solution was then filtered and evaporated on the water bath, a white crystalline solid was again left. Investigation of the activated charcoal showed that concentrated sulfuric acid extracted some material which was brown down in a few minutes while precipitates on heating likewise with ammonia. Therefore another sample of the activated charcoal was boiled with concentrated sulfuric acid, filtered, and the charcoal washed three times with water and not decolorized well. A sample of a specially prepared charcoal for geophysical purposes manufactured by the Harnsby-Goway Co. was obtained and tested but was unsuccessful; the color was not removed. Industrial earth, known as "Sil-o-neo" were also tried unsuccessfully; Fuller's earth made a very clear solution but no color was removed. Some of the brown viscous solution was dissolved in water, the solution filtered and evaporated to a constant volume (estimated when no more vapor could be seen to come) under diminished pressure (water pump) until it became more brown. It was then allowed to cool, and dry hydrochloric acid gas passed in, lines to expel all air or other vapor

present, and then under pressure. The solution became slightly warm. A few fine crystals formed on the interior surface of the flask where some of the solution had spattered during distillation, which however were quite indistinct and seemed to be in the center of a drop of water or solution. On allowing the flask to stand over night the whole of the solution seemed to be filled with crystals. There were too indistinct to enable their crystalline form to be determined so an attempt was made to remove some for examination. As soon as they came into contact with the air they disappeared and left a very viscous solution, indicating that they are very hygroscopic. A small amount was removed and placed in a dish in a vacuum dessicator which was evacuated and left for a month, with periodical examinations. No solid appeared at any time.

This is as far as the investigation has been carried at the present time, April twenty-fifth, but its study is being continued.

pressure, and then under pressure. The solution became slightly warm. A few fine crystals formed on the interior surface of the flask where some of the solution had evaporated during distillation, which however were quite insignificant and seemed to be in the center of a drop of water or solution. On allowing the flask to stand over night the whole of the solution seemed to be filled with crystals. There were too numerous to count and their crystalline form to be determined. An attempt was made to remove some for examination. As soon as they came into contact with the air they disappeared and left a very viscous solution, indicating that they are very hygroscopic. A small amount was removed and placed in a dish in a vacuum desiccator which was evacuated and left for a month, with periodical examinations. No solids appeared at any time.

This is as far as the investigation has been carried at the present time, April twenty-fifth, but the study is being continued.

Conclusion

The results of this investigation may be briefly summarized as follows:

- (1) Ortho toluidine may be easily converted into its sulphonic acid in which the sulphonic acid group is in the position meta to the methyl group.
- (2) Para toluidine is converted into a mixture of two isomeric sulphonic acids of which the one with the sulphonic acid group in the position meta to the methyl group is obtained in a ten per cent yield.
- (3) Ortho toluidine sulphonic acid may be easily diazotized using sodium nitrite and concentrated hydrochloric acid.
- (4) The diazo compound is very stable.
- (5) The diazo compound is easily decomposed with n-butyl alcohol, the hydrogen reaction taking place.

Conclusions

The results of this investigation may be briefly

summarized as follows:

- (1) Ortho toluidine may be easily converted into its sulfonic acid in which the sulfonic acid group is in the para position to the methyl group.
- (2) Para toluidine is converted into a mixture of two isomeric sulfonic acids of which the one with the sulfonic acid group in the para position to the methyl group is obtained in a ten per cent yield.
- (3) Ortho toluidine sulfonic acid may be easily diazotized using sodium nitrite and concentrated hydrochloric acid.
- (4) The diazo compound is very stable.
- (5) The diazo compound is easily decomposed with n-butyl alcohol, the hydrogen reaction taking place.

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